



CONFIDENTIAL

50X1-HUM

$[\text{Ga}(\text{OH})_4]^-$  and  $\text{Li}_2\text{O} \cdot \text{Ga}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , respectively. Further heating results in the final, irreversible dehydration to  $\text{Li}[\text{GaO}_2]$ ; fusing with  $\text{Li}_2\text{SO}_4$  at  $1,000-1,100^\circ$  for 20 hours gives rounded crystals, hardly soluble in  $\text{H}_2\text{O}$ .

(2) Solution of  $\text{Ga}(\text{OH})_3$  in excess  $\text{NaOH}$  gives a product with  $\text{Na}:\text{Ga}=1:1$ . With a deficit of  $\text{NaOH}$ , evaporation gives a sirupy mass which can only be made to solidify over  $\text{P}_2\text{O}_5$  or by boiling with absolute alcohol for 3 hours; the latter operation gives a product of the composition  $\text{Na}[\text{Ga}(\text{OH})_4]$  but not in well-formed crystals. Calcination of finely ground  $\text{Ga}_2\text{O}_3$  with  $\text{Na}_2\text{CO}_3$  in a Pt crucible at  $850-1,000^\circ$ , 15-30 minutes, gives  $\text{Na}[\text{GaO}_2]$ ; excess carbonate remains unchanged. The  $\text{Na}[\text{GaO}_2]$  plates dissolve in  $\text{H}_2\text{O}$  easily without significant hydrolysis; they are easily hydrated to  $\text{Na}[\text{Ga}(\text{OH})_4]$ , which is reversibly dehydrated at  $140^\circ$ , 40 minutes; thermography showed that this dehydration takes place at  $117-20^\circ$ ; there also appears an as yet unexplained endothermal effect at  $170^\circ$ .

(3)  $\text{K}[\text{Ga}(\text{OH})_4]$  was prepared by dissolving 1.5 g  $\text{Ga}(\text{OH})_3$  in 10 ml 50%  $\text{KOH}$  and long evaporation over  $\text{H}_2\text{SO}_4$ ; monoclinic or triclinic crystals, density 2.56,  $n_D 1.509$ ,  $n_D 1.485$ . Heating to  $300^\circ$  results in  $\text{K}[\text{GaO}_2]$ ,  $n_D 1.500$ , heating to  $400^\circ$ , in  $\text{K}[\text{GaO}_2] \cdot \text{H}_2\text{O}$ . The last  $\text{H}_2\text{O}$  is hard to eliminate at higher temperature.

(4) Pure  $3\text{CaO} \cdot \text{Ga}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ , or  $\text{Ca}_3[\text{Ga}(\text{OH})_6]_2 \cdot 6\text{H}_2\text{O}$ , was obtained by adding a solution of  $\text{Na}[\text{Ga}(\text{OH})_4]$  to a boiling saturated solution of  $\text{Ca}(\text{OH})_2$ ; hexagonal plates, density 2.38,  $n_D 1.53$ ,  $n_D 1.515$ . Addition of a solution of  $\text{Na}[\text{Ga}(\text{OH})_4]$  to a cold saturated solution of  $\text{Ca}(\text{OH})_2$  gives fine crystalline spherulites of density 2.35, mean  $n_D 1.565$ , analyzing  $4\text{CaO} \cdot \text{Ga}_2\text{O}_3 \cdot 23.5\text{H}_2\text{O}$ . No precipitation occurs on adding  $\text{Na}[\text{Ga}(\text{OH})_4]$  to 20%  $\text{CaCl}_2$ ; however, addition of  $\text{NH}_4\text{OH}$  does precipitate  $4\text{CaO} \cdot \text{Ga}_2\text{O}_3 \cdot 21\text{H}_2\text{O}$  (analogous to the Al compound), fine spherulitic crystals. Reaction between  $\text{CaCl}_2$  and warm  $\text{K}[\text{Ga}(\text{OH})_4]$  gives impure cubic crystals strongly contaminated with  $\text{Ca}(\text{OH})_2$  and resembling  $\text{Ca}_3[\text{Al}(\text{OH})_6]_2$ .

(5) No precipitation occurs between dilute  $\text{K}[\text{Ga}(\text{OH})_4]$  and dilute  $\text{SrCl}_2$  but addition of the latter to hot concentrated  $\text{Sr}(\text{OH})_2$  precipitates  $\text{Sr}_3[\text{Ga}(\text{OH})_6]_2$ , rhombic dodecahedra, density 3.54,  $n_D 1.625$ .

"Chemistry of Gallium: III. Thiogallates of alkali Metals," B. N. Ivanov-Kain, Ya. I. Pabovik, Moscow Inst Fine Chem Tech from M. V. Lomonosov

"Zhur. Obshch. Khimii" Vol 17, 1947, pp 1247-52

(1)  $\text{Li}_2\text{CO}_3$  (or  $\text{Na}_2\text{CO}_3$ ) in equimolecular mixture with  $\text{Ga}_2\text{O}_3$ , heated in a stream of dry  $\text{H}_2\text{S}$ , 2-3 l/hour, 2 hours at  $800^\circ$ , then 4 hours at  $900^\circ$ , and cooled under  $\text{H}_2\text{S}$ , gave light-brown masses with distinct crystalline structure:  $\text{Li}_2[\text{Ga}_2\text{S}_4]$ , brown-red, melting at  $1,020 \pm 50^\circ$ , apparently rhombic plates and prisms, highly birefringent,  $n > 1.78$ , density 2.98, does not react with boiling  $\text{H}_2\text{O}$ ;  $\text{Na}_2[\text{Ga}_2\text{S}_4]$ , dark yellow, melting at

- 2 -

CONFIDENTIAL

CONFIDENTIAL

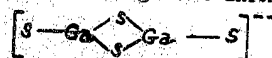
50X1-HUM

$952^\circ \pm 2^\circ$ , tetragonal prisms, highly birefringent,  $n > 1.78$ , density 2.86, partly soluble in  $H_2O$ , going over into  $Na_2[Ga_2S_4] \cdot 2H_2O$  on moistening and drying over  $CaCl_2$ .

(2)  $Ga_2O_3$  was heated with eight parts  $K_2CO_3$  ( $Rb_2CO_3$ ,  $Ca_2CO_3$ ) and eight parts S under  $CO_2$ , 15 minutes at  $450^\circ$ , then 2-3 minutes at  $1,100^\circ$ , leached with  $H_2O$ , and the insoluble thiogallates were washed with  $H_2O$  and alcohol and dried over  $CaCl_2$ :  $K_2[Ga_2S_4]$ , tetragonal, melting at  $965^\circ \pm 2^\circ$ , yellow, medium birefringence,  $n > 1.74$ , does not react with  $H_2O$ ;  $Rb_2[Ga_2S_4]$ , yellow-brown tetragonal, melting at  $960^\circ \pm 2^\circ$ , highly birefringent,  $n > 1.78$ , density 3.42;  $Ca_2[Ga_2S_4]$ , rhombic, light yellow to bright red pleochroic, melting at  $980^\circ \pm 5^\circ$ , highly birefringent,  $n > 1.78$ , density 3.56, does not react with  $H_2O$ . Li and Na thiogallates cannot be prepared by this method, only by (1).

(3) All thiogallates are stable in air; they are decomposed by strong acids with evolution of  $H_2S$ .

(4) By the thiogallate anion type,



Ga differs from Al and shows an analogy with In and Tl, evidently owing to the 18-electron shell of the ion, in contrast to the eight outer electrons of  $Al^{+++}$ .

"Kinetics of the Decomposition of Lithium Amalgam in Water, and in Aqueous Solutions of Lithium Chloride and Lithium Hydroxide," S. I. Sklyarenko, B. A. Sakharov, Moscow Inst Fine Chem Tech imeni M. V. Lomonosov

"Zhur Obshch Khimii" Vol 17, 1947, pp 1385-400

(1) The rate of solution of Li from its amalgam, in agitated  $H_2O$  maintained at a constant pH = 9 by constant neutralization with HCl at a rate corresponding to that of the solution, follows the law  $-dc/dt = k_1 s \sqrt{c}$ , where  $c$  = concentration of Li in the amalgam at the time  $t$  (minutes),  $s$  = surface area of the amalgam in square centimeter, in agreement with Fletcher and Kilpatrick; with  $s = 9.60$  sq cm, volume of amalgam 4 ml, volume of  $H_2O$  60 ml, at  $20^\circ$ , stirring at 300 rpm, initial concentrations  $c_0$  0.270-0.633 M,  $k_1 = 1.05 \times 10^{-4}$ .

(2) This law does not hold if the pH is allowed to rise freely with progressing solution of the Li; in that case, the rate is expressed by  $t - t_1 = (2.303/k_2) \log (c_0/c)$ , where  $t_1$  = the time (minutes) of attainment of the same  $c$  under conditions of constancy of pH = 9; from measurements of the progress of the solution by the volume  $v$  of  $H_2$  evolved, with  $c_0 = 0.550$  M corresponding to 25.0 ml  $H_2$  (complete extraction of the Li),  $k_2 = 1.72$  at  $20^\circ$  and  $300$  rpm. The effect of the temperature, at constant rate of stirring and  $c_0 = 0.455$  M, is illustrated by the data: 20, 30, 50, and  $60^\circ$ , after 4 minutes  $v = 6.5, 8, 12$ , and 15 ml, after 8 minutes  $v = 12.5, 14.5, 18.5$ , and 20 ml; at  $20^\circ$ , rates of stirring 0, 300, and 450 rpm, after 8 minutes

- 3 -

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

$V = 12, 15.5$  and  $17$  ml.

(3) Extraction of Li by LiOH solutions sufficiently concentrated for the change of alkalinity in the course of the reaction to be negligible, again follows the  $\sqrt{t}$  law as under (1); at  $20^\circ$ ,  $300$  rpm,  $c_0 = 0.600-0.650$ , initial LiOH =  $0, 0.46, 0.85, 1.80, 2.40$ , and  $4.82$  M,  $10^4 \times k_1 = 1.05, 0.57, 0.37, 0.112, 0.090$ , and  $0.046$ ; in terms of temperature, at  $20, 40$ , and  $60^\circ$ , with  $c_0 = 0.616$  M, initial LiOH  $1.80$  M,  $10^4 \times k_1 = 0.112, 0.262$ , and  $0.561$ .

(4) The acceleration of the extraction by contact of the amalgam with low-overpotential metals, is illustrated by the data (exposed surface area of the amalgam  $7.5$  sq cm, of the metal  $2.0$  sq cm,  $20^\circ$ , initial LiOH  $2$  M): contact none, Fe-Cb, Fe-Zr, cast Fe, graphite, time of complete decomposition  $180, 1.3, 2.5, 3.5, 4.5$  minutes.

(5) The  $\sqrt{t}$  law holds also for extraction by LiCl solutions; at  $20^\circ$   $c_0$   $0.6$  M, LiCl  $4, 8$ , and  $10$  M,  $10^4 \times k_1 = 0.890, 0.690$ , and  $0.320$ ; at  $50^\circ$ , LiCl  $10$  M,  $10^4 \times k_1 = 0.650$ .

"Structural Changes in Rubber by the Action of Molecular Oxygen: II. Kinetics of the Destructive Solution of Vulcanized Rubber," B. Dogadkin, Z. Tarasova, Moscow Inst Fine Chem Tech imeni M. V. Lomonosov

"Zhur Obshch Khimii" Vol 17, 1947, pp 1401-14

Proof was sought and obtained of the indispensability of O for solution of vulcanized rubber and, consequently, of the mainvalence nature of vulcanisation, as opposed to the intermolecular forces theory advocated by Williams on the basis of his peptization experiments. A mixture of smoked sheet 100, S 2 tetramethylthiuram disulfide 0.2, ZnO 1, and stearic acid 1, was vulcanized at  $141^\circ \pm 0.5^\circ$  (optimum in 20 minutes) with the characteristics: CHCl<sub>3</sub> extract 0%, Me<sub>2</sub>CO extract 3.8%, combined S 1.6%, tensile strength 190-200 kg/sq cm, elongation 900%. Vulcanisation was carried out on thin layers coated (in O-free C<sub>6</sub>H<sub>6</sub> solution) on the outer surface of a cylindrical glass ampul in the absence of O(CO<sub>2</sub> atmosphere); the vulcanized product was then extracted with cold CHCl<sub>3</sub> in the dark and in a current of pure N for 16 hours, and the ampul carrying the film was immersed in a thermostated closed vessel filled with xylene and equipped with a reflux condenser to prevent losses of solvent by the stream of gas bubbled through the vessel at a constant rate. Progress of the solution was observed by microbalance weighings of ampul and film. Full details given.

"Pilocarpine Alkaloids: II. Synthesis of Racemic Acetropypilocarpine," A. G. Matradze, E. E. Mikhlin, Moscow Inst Fine Chem Tech imeni M. V. Lomonosov

- 4 -

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

"Zhur Obshch Khimii" Vol 17, 1947, pp 1718-27

Isovaleric Acid (160 g) and 80 g  $\text{PCl}_3$  were heated to  $60^\circ$ , then treated with 300 g Br and heated until decolorized; the solution, slowly added with stirring to 147 g absolute EtOH and treated with ice. Full details necessary to synthesize end product are available.

"Isoquinoline Compounds: Synthesis of 2-Methyl-1-(4-Methoxybenzyl) - 6 - Methoxy - 1, 2, 3, 4 - Tetrahydroiso-Quinoline Methiodide," R. S. Livshits, G. I. Bazilevskaya, M. S. Bainova, O. E. Dobrovinskaya, N. A. Preobrazhenskiy, Moscow Inst Fine Chem Tech imeni M. V. Lomonosov

"Zhur Obshch Khimii" Vol 17, 1947, pp 1671-7

$\text{HOC}_6\text{H}_4\text{CHO}$  (25 g), added with stirring to 8.6 g NaOH in 75 cc MeOH and the warm solution treated with 38.7 g  $\text{Me}_2\text{SO}_4$ , keeping the mixture at gentle reflux, with additions of alcohol NaOH to maintain alkalinity, yielded 88% 3-methoxybenzaldehyde,  $b_p$  117-180,  $d_{20}^{25}$  1.115,  $n_D^{25}$  1.5227. This (20 g), 32 g malonic acid, 50 cc pyridine, and 1 cc piperidine, kept 1 hour at  $80^\circ$ , 2 hours at  $100^\circ$ , and 0.5 hours at gentle reflux, then poured into 230 cc 12% HCl, gave 3-methoxycinnamic acid, melting at  $117^\circ$  (94%). This (10 g) and 400 g 4% Na-Hg in 400 cc  $\text{H}_2\text{O}$ , kept 10-12 hours at  $100^\circ$  and the filtered solution acidified with HCl, gave 86%  $\beta$ -(2-methoxyphenyl) propionic acid, melting at  $48-90^\circ$  (crude); melting at  $50^\circ$  (from  $\text{H}_2\text{O}$ ). This boiled 8 hours with MeOH in the presence of  $\text{H}_2\text{SO}_4$  gave 91% Me ester, melting at  $29-30^\circ$ ,  $b_p$  140-150. This (24 g), shaken 10-12 hours with 325 cc saturated aqueous  $\text{NH}_4\text{OH}$  and concentrated in vacuo, gave 99% of the amide, melting at  $55-60^\circ$ ,  $b_p$  218-190. This (20 g) with KOH gave 60% 3-methoxyphenethylamine (I),  $b_p$  118-190 (rapidly forms a solid carbonate in the air). To 40 g 4-MeOC<sub>6</sub>H<sub>4</sub>CHO in 90 cc 96% EtOH and 75 cc 40% formalin was added 105 cc 55% KOH solution below  $60^\circ$  and the mixture heated 1 hour at  $65-70^\circ$  and boiled 20 minutes; concentration in vacuo and extraction with Et<sub>2</sub>O (washed with NaHSO<sub>4</sub> solution) gave 87.5% 4-methoxybenzyl alcohol,  $b_p$  1430. This (35 g), added to 44 g  $\text{SOCl}_2$  below  $10^\circ$  and after 1 hour treated with 1.5 g chalk and 50 cc Et<sub>2</sub>O and allowed to stand overnight, gave 92% 4-methoxybenzyl chloride,  $b_p$  111-120. This (35 g) in 70 cc benzene, treated with stirring with 33.7 g KOH in 135 cc warm water and kept 7 hours with stirring at  $75-80^\circ$ , gave 72% 4-methoxybenzyl cyanide,  $b_p$  157-80. This (24 g), 72 cc 96% EtOH, and 40 cc 50% KOH, stirred 7 hours at  $100^\circ$ , concentrated, diluted with water, and acidified with cooling with 20% HCl, gave 4-methoxyphenylacetic acid, melting at  $86.50^\circ$  (fr. heptane) (yield, 86.8%); its Et ester (II),  $b_p$  136-7,  $d_{20}^{25}$  1.0970,  $n_D^{25}$  1.5070, was prepared in 87.4% yield by boiling with EtOH in the presence of  $\text{H}_2\text{SO}_4$ . I (5 g), 6.43 g II, and 0.5 g pyridine,

5 -

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

heated 3 hours at 180°, allowed to stand overnight, and triturated with ligroin, gave 67.6% N-(3-methoxyphenethyl) (4-methoxyphenyl) acetamide, melting at 80° (from CHCl<sub>3</sub>-ligroin). This (2 g) and 18 g POC<sub>l</sub><sub>3</sub> kept 2 hours at 100°, then allowed to stand overnight and poured onto ice, the heavy oil extracted several times with a small volume of hot water, and the extract treated with charcoal, made alkaline with 40% NaOH with cooling, and extracted with benzene, gave 74% 1-(4-methoxybenzoyl)-6-methoxy-3,4-dihydroisoquinoline, melting at 155.5-6° (from EtOH); HCl salt, melting at 167-8°; picrate, melting at 168-9° (from AcOH). The base (2.8 g) heated 6 hours in 28 cc MeI gave 86.95% methiodide, melting at 168° (from EtOH). The latter (2 g) in 55 cc warm concentrated HCl and 25 cc water was treated with 7.5 g Zn dust over 1 hour with stirring, then stirred at 90° until the Zn dissolved; addition of NH<sub>4</sub>OH and extraction with Et<sub>2</sub>O gave 77.5% 2-methyl-1-(4-methoxybenzyl)-6-methoxy-1,2,3,4-tetrahydroisoquinoline, melting at 63.5° (from 70% EtOH); HCl salt, melting at 190°; picrate, melting at 179° (from AcOH); methiodide, melting at 185-6° (from EtOH). This product, having a structure analogous to that of curare alkaloids, was prepared for physiological studies.

"Vulcanization Accelerators in the Polysulfide Series, II," S. S. Livshits, N. A. Preobrazhenskiy, Moscow Inst Fine Chem Tech imeni M. V. Lomonosov

"Zhur Obshch Khimii" Vol 17, 1947, pp 1706-9

Pipecoline (0.5 g) in 20 cc Et<sub>2</sub>O treated with cooling and stirring with 0.23 g NaOH in 0.4 cc H<sub>2</sub>O, followed by 0.44 g CS<sub>2</sub> in 5 cc Et<sub>2</sub>O, gave 1 g Na 2-pipecolinedithiocarbamate, melting at 117-19°; after drying over P<sub>2</sub>O<sub>5</sub>, it melts at 215°. Zn salt, melts at 193-4°, soluble in benzene. The Na salt (0.4 g) in 30 cc Et<sub>2</sub>O was treated with 0.15 g S<sub>2</sub>Cl<sub>2</sub> in 5 cc Et<sub>2</sub>O with stirring; removal of Et<sub>2</sub>O and evaporation in vacuo yielded 0.25 g 2-pipecolinethiuram tetrasulfide, decomposition 37°. 3-Pipecoline (0.5 g) in 20 cc Et<sub>2</sub>O was stirred with 0.23 g NaOH in 0.45 cc H<sub>2</sub>O, followed by 0.44 g CS<sub>2</sub> in 5 cc Et<sub>2</sub>O with cooling; after stirring 1 hour, concentration in vacuo and addition of Et<sub>2</sub>O gave 1 g Na 3-pipecolinedithiocarbamate, melting at 199-200° (from EtOH-Et<sub>2</sub>O); Zn salt (from the Na salt and Zn acetate), melting at 204-5° (from benzene and Et<sub>2</sub>O). The Zn salt (1 g) in 25 cc Et<sub>2</sub>O stirred 3-4 hours with 0.37 g S<sub>2</sub>Cl<sub>2</sub> in 5 cc Et<sub>2</sub>O, gave 93.3% 3-pipecolinethiuram hexasulfide, melting with 107-8° (from CS<sub>2</sub>-Et<sub>2</sub>O). 4-Pipecoline (0.5 g) in 2 cc Et<sub>2</sub>O added to 0.17 g CS<sub>2</sub> in 1 cc cold Et<sub>2</sub>O gave 92.9% 4-pipecoline 4-pipecolinedithiocarbamate, melting at 155-6° (from EtOH); the Na salt made analogously to that of 2-pipecoline, melting at 200-1° (from EtOH-Et<sub>2</sub>O); Zn salt, melting at 219-19.5° (from benzene); Cd salt, amorphous, high-melting solid, almost insoluble in the usual original solvents. The Na salt (0.5 g) in 15 cc Et<sub>2</sub>O treated with cooling with 0.2 g S<sub>2</sub>Cl<sub>2</sub> in 5 cc Et<sub>2</sub>O, stirred 1 hour, and filtered gave 4-pipecoline-

- 6 -

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

thiuram tetrasulfide, melting at 104-4.5° (from CS<sub>2</sub>; 57.7%); if an excess (30-50%) of S<sub>2</sub>Cl<sub>2</sub> is used, the product is doughlike.

- E N D -

- 7 -

CONFIDENTIAL